

NEW TECHNIQUES FOR THERMOCHEMICAL PHASE EQUILIBRIUM PREDICTIONS IN COAL ASH SYSTEMS

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ABSTRACT

PHOEBE is a new computer code developed at UNDEMRC as a part of a long-term study of coal ash deposition phenomena in combustion systems. The task of developing a new code was undertaken to eliminate the various problems encountered with existing phase equilibrium codes such as SOLGASMIX and PACKAGE. These codes were not able to produce satisfactory comparisons with experimental data and the goal of PHOEBE was to apply better techniques to calculate the minimum Gibbs free energy at thermodynamic equilibrium. The new PHOEBE algorithm has been rigorously tested against standard mathematical functions and is currently being tested against experimental data on coal ash slags. This paper discusses the minimization and optimization techniques used in PHOEBE.

I. Introduction

Understanding the behavior of inorganic constituents during coal combustion is needed to predict the development of ash deposit formation, slagging, and fouling in a combustor. This requires information on the formation of the various mineralogical phases in the vapor, liquid, and solid states and their relationship to the relative amounts of the inorganic elements present in the raw coal and to the variations in combustion conditions. With this type of data, a better understanding of not only the deposition processes but their mitigational aspects as well may be achieved. The calculation of the equilibrium species and phase distributions provides a good starting point in approximating the requisite data.

The problem of obtaining the equilibrium values (x^*_1, \dots, x^*_n) of n distinct species comprising a thermodynamic system S at a fixed temperature and pressure has been extensively addressed in the past, and the utility of obtaining the equilibrium values by minimizing the Gibbs free energy of the system has also been thoroughly emphasized (1-10). A variety of numerical packages (HALTAFALL, SOLGASMIX, PACKAGE, SHIMPO-GOTO, NASA-CEC, etc.,) related to this problem have been reported in the literature and their relative merits also discussed. Although the majority of these packages seem to perform adequately on many test cases, they sometimes also appear to produce quite erroneous results. (It must be pointed out that our experience with the above-mentioned packages is limited primarily to SOLGASMIX.) This is not unexpected, since conventionally, the calculations are simplified to the extent that the various interaction terms in the Gibbs free energy of the system are represented only by the 'free energy of mixing' terms, all other interactions being assumed minimal or nonexistent. It has been argued very convincingly that it is indeed valid to approximate the activities of the species by their respective mole fractions (11-13). Nonetheless, this minimality assumption has important consequences for the stability (and hence the existence) of various phases within the

system: even the introduction of a simple Lennard-Jones type potential in a non-interactive system, it may be recalled, lowers the energy of the system, favors the formation of the liquid phase, and would perhaps be more representative of the correct free energy of the system.

This in turn leads to the problem of the availability, or lack thereof, of thermochemical data. The most widely referred sources of thermodynamic data (16-18) often lack data for many of the typical products in coal combustion systems. It is to be also noted that the available thermodynamic tables are themselves extrapolated so that further extrapolations to unreferenced compounds may lead to additional sources of error.

The organization of the paper then is as follows. In Section II the mass constrained Gibbs free energy minimization problem is discussed in detail. A variety of standard numerical methods currently available and their relative merits are also briefly discussed. Section III describes PHOEBE, a Gibbs free energy minimization program currently under development at UNDEMRC.

II. Mass-Constrained Gibbs Free Energy Minimization

Let S be a multicomponent thermodynamic system at a given temperature T and pressure P comprising the species X^1, \dots, X^n and let G be Gibbs free energy of S . Let

$$A^{\alpha}_{aj} x^j_{\alpha} = b_a \quad 1)$$

be the mass constraint relations for S where

A^{α}_{aj} = stoichiometry coefficient of atom (or element) a in species j in phase α ,

x^j_{α} = the number of moles of species j in phase α ,

b_a = the number of moles of atom (or element) a .

In Equation 1 the index α ranges from 1 through the number of phases N_p , the index j ranges from 1 through the number of species N_s , and the index a ranges from 1 through the number of atoms or elements N_a . The Einstein summation convention is used in Equation 1 and in the rest of the paper. Implicit in Equation 1 are the nonnegativity requirements,

$$x^j_{\alpha} \geq 0, \quad 1 \leq j \leq N_s, \quad 1 \leq \alpha \leq N_p, \quad 2)$$

that need to be satisfied by the molar amounts of the various species in the system. The Gibbs free energy of S is written as

$$G = \sum_{\alpha} \sum_j x^j_{\alpha} \mu^{\alpha}_j \quad 3)$$

where the μ^{α}_j are the chemical potentials of the species which are in turn approximated as follows: let,

$$x_{\alpha} = \sum_{j=1}^{N_s} x_{j\alpha} \quad 4)$$

be the total number of moles in phase α , and $(\mu_o)^{\alpha_j}$ the standard chemical potential of species j in phase α . μ^{α_j} is then given by

$$\mu^{\alpha_j} = \left\{ \begin{array}{ll} x_{j\alpha}(\mu_o)^{\alpha_j} & , \text{ if } \alpha \text{ is a pure condensed phase} \\ x_{j\alpha}(\mu_o)^{\alpha_j} + x_{j\alpha} \ln \left[\frac{P x_{j\alpha}}{x_{\alpha}} \right] & , \text{ if } \alpha \text{ is a gas phase} \\ x_{j\alpha}(\mu_o)^{\alpha_j} + x_{j\alpha} \ln \left[\frac{x_{j\alpha}}{x_{\alpha}} \right] & , \text{ if } \alpha \text{ is a solid-liquid mixture} \end{array} \right\} \quad 5)$$

Note that, in Equation 5 the indices α and j are free indices and all implied summations over α and j are to be disabled.

Equations 3-5 approximating the Gibbs free energy of the system are for an assumed or *a priori* phase distribution. For the system S containing N_a distinct elements and N_p distinct phases the Gibbs phase rule may be written as

$$F = (N_a - r - 1) - N_p \quad 6)$$

with F denoting the number of degrees of freedom and r denoting the rank of the stoichiometry matrix $A^{\alpha_{aj}}$. The nonnegativity requirement

$$F \geq 0 \quad 7)$$

on the degrees of freedom of the system then upper bounds the maximum number of extant phases at equilibrium according to

$$1 \leq N_p \leq N_a - r - 1, \quad 8)$$

and the system attains a free energy value G^* at equilibrium which is minimal with respect to both the possible phase distributions and the possible molar amounts of the species, the latter subject to the mass constraints in Equation 1. Hence, with P denoting the set of all possible phase distributions, which in view of Equation 8 is finite, and $G^{(p)}$ denoting the Gibbs free energy of S for a particular phase distribution $p \in P$, the mass constrained Gibbs free energy minimization problem takes the mathematical form

$$\text{Fin} \min_{p \in P} \inf \{ G^{(p)}(x_1^1, \dots, x_{N_p}^{N_s}) \mid (x_1^1, \dots, x_{N_p}^{N_s}) \in \mathbb{R}^{N_s N_p}, A^{\alpha_{aj}} x_{j\alpha} = b_a \}. \quad 9)$$

We wish to stress a couple of aspects regarding Equation 9. Firstly, it may be argued from purely physical considerations that there must exist a unique set x^{*1}, \dots, x^{*N_p} of molar values of the species that provides the correspondingly unique minimal of equilibrium value G^* of the free energy. At the mathematical level, the set

$$\Omega = \{(x^1_1, \dots, x^{N_s}_{N_p}) \in \mathbb{R}^{N_s N_p} \mid A^{\alpha}_{aj} x^j_{\alpha} = b_a, x^j_{\alpha} \geq 0, 1 \leq j \leq N_s, 1 \leq \alpha \leq N_p\} \quad (10)$$

is a compact (closed and bounded) convex subset of the $N_p N_s$ -dimensional real number space $\mathbb{R}^{N_s N_p}$. The Gibbs free energy G as approximated in Equations 3-5 is a concave, smooth (i.e., infinitely differentiable) function on the positive hyperoctant of $\mathbb{R}^{N_s N_p}$ and hence in the interior of Ω . A theorem of Kuhn and Tucker (19) then asserts that any local minimizer of Equation 9 is the global minimizer, i.e., that there exists one and only one minimizer for 9. Further, this unique minimizing point is given by (20-22)

$$x^{*j}_{\alpha} = \lim_{\lambda \rightarrow \infty} \frac{\int_{\Omega} x^j_{\alpha} e^{-\lambda G}}{\int_{\Omega} e^{-\lambda G}} \quad (11)$$

In physical terms, interpreting λ as time, Equation 11 merely expresses the fact that the equilibrium mole values of the species are given in the asymptotic limit $\lambda \rightarrow \infty$ of their expectation or average values.

The second aspect regarding Equation 9 that needs to be stressed is that of the minimization over the possible phase distributions. The total number of possible phase distributions or equivalently the cardinality $|P|$ of the set P is bounded above by

$$|P| \leq \sum_{N_p=1}^{N_a-r-1} \sum_{\substack{N_{k_1} + \dots + N_{k_t} \leq N_s \\ (N_{k_1}) \dots (N_{k_t})}}^{N_s} \quad (12)$$

The estimate in Equation 12 is conservative and in practice the total number of phase distributions actually realized are considerably lower. Despite this, for a fairly large system ($N_s \geq 50$, $N_a \geq 10$), the phase distribution count grows very rapidly and the problem becomes computationally intractable. Various schemes are being studied and a few important results obtained in this regard. A report on these results will soon be appearing in a forth-coming paper (31). The perhaps most interesting trend that we have observed so far in our numerical studies is that the species appear to behave in the manner of 'bosons' preferring to occupy an already existing phase rather than 'creating' a new one. Our more recent studies are expected to shed further light on this rather intriguing aspect of the problem.

III. PHOEBE

A computer program called PHOEBE for calculating the equilibrium mole values and the Gibbs free energy of a given thermodynamic system has been developed implementing the ideas discussed above. PHOEBE is intended primarily for personal computer use and is fully menu driven. The user generates a specific thermodynamic system from a large database and the equilibrium evolution for the system as a function of temperature can be studied. The average run time for a system comprising approximately 50 species and 10 elements over a range of 10-12 temperatures is about 2 hours. There are no restrictions on the number of species or elements or phases except as dictated by available memory. A mainframe version of PHOEBE is currently under development.

The minimization algorithm adopted is a combination of the "variable metric" algorithms (23) and the projection gradient method (24). Given a point $x^{(0)}$ in the interior of the feasible region Ω , a sequence $\{x^{(n)} | n \in \mathbb{N}\}$ is generated converging to a local (and by convexity, to the global) minimum of G . If $M^{(k)}$ denotes the constraint matrix of the subset of constraints currently active at iteration step k , the idempotent projection matrix P (superscript T denotes matrix transpose),

$$P = I - M^{(k)T} (M^{(k)} M^{(k)T})^{-1} M^{(k)} \quad (13)$$

is constructed to project the gradient of G into the orthogonal complement of the kernel of $M^{(k)}$. It may be observed that the projection matrix P in Equation 13 reduces to the identity matrix when restricted to the kernel of $M^{(k)}$. It should also be observed that if the sequence of points so generated is a sequence of regular points (25) of Ω the first order optimality conditions are satisfied (26). If non-regular or degenerate points are encountered in the generation of the sequence leading to the so-called degeneracy or linear dependency problem, these degenerate points need to be appropriately 'sidestepped' (27),(28). (In any event, a generalized inverse of $M^{(k)} M^{(k)T}$ may be made use of to enter the orthogonal subspace of the kernel of $M^{(k)}$.) The convergence of the sequence is accelerated in its later stages by utilizing the Hessian of G , or if the problem is too large, by approximating the Hessian by a suitable symmetric positive definite matrix. The rate of convergence varies between being linear and superlinear.

In addition to the real Hermiticity of the active or binding constraint matrix $M^{(k)} M^{(k)T}$, its nonnegativity, meaning that each matrix element of $M^{(k)} M^{(k)T}$ is nonnegative, has some important consequences. The eigenvalues of $M^{(k)} M^{(k)T}$ are all real, and in view of the Perron-Frobenius theorems (29-30), the positive eigenvalues are all distinct with the largest positive eigenvalue bounded below by the minimum of the row sums and bounded above by the maximum of the row sums. Also, the existence of a nonnegative eigenvector with eigenvalue equal to the spectral radius of $M^{(k)} M^{(k)T}$ may be asserted. These remarks apply to the Hessian of G as well and are actively utilized in resolving the degeneracy problem if and when it arises.

IV. Conclusions

We have been able to develop a fairly satisfactory algorithm for obtaining numerical solutions to the mass-constrained Gibbs free energy minimization problem. PHOEBE performed quite satisfactorily in test runs on known binary and ternary systems. Some coal systems have also been analyzed and excellent results obtained. However, a few of the coal systems analyzed also produced unrealistic results which led directly to the identification and resolution of the degeneracy problem discussed earlier. Our current attempts are now directed towards representing the free energy of the system more accurately and towards accelerating the convergence of the iterative scheme. We expect to detail these extensions and include comparative studies of program output and experimental data in a forthcoming paper (31).

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